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(54) Slurry Phase Syngas Conversion Process

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Abstract of the Disclosure

In converting syngas to hydrocarbons in a slurry phase reactor using an iron-based Fischer-Tropsch catalyst slurried in an inert solvent, enhanced conversion of the syngas is obtained by adding particulate sodium, potassium or barium carbonate to the slurry phase.

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SLURRY PHASE SYNGAS CONVERSION PROCESS

Field of the Invention

This invention relates to a process for converting syngas to hydrocarbons by contacting a Fischer-Tropsch catalyst in a slurry phase which additionally contains slurried therein sodium, potassium or barium carbonate.

Background of the Invention

10 During the conversion of syngas to hydrocarbons, many techniques are known for contacting the syngas with the appropriate catalyst. For example, a packed bed of catalyst can be utilized as well as a fluidized bed. Alternatively, the catalyst can be slurried in appropriate organic solvents and the syngas bubbled there-
through. The use of this slurry phase process provides certain advantages. For example, additives may be added to the slurry phase to change the reactivity of the catalyst. In certain cases these additives may be difficult to incorporate directly into the catalyst, or they may readily leach out of the catalyst by contact with the reaction products. Utilization of the slurry phase pro-
cess can alleviate some of these problems.

20 Summary of the Invention

The instant invention relates to a process for converting syngas (carbon monoxide and hydrogen) to hydrocarbons, which process comprises contacting the syngas with an iron-based Fischer-Tropsch catalyst wherein said catalyst is dispersed as a slurry in an inert organic solvent and wherein additionally sodium carbonate, potas-
sium carbonate, barium carbonate or mixtures thereof are also



dispersed as a slurry in an inert organic solvent. The use of these additives to the slurry phase provides for enhanced conversion of syngas to hydrocarbon products. The use of other carbonates such as for example, magnesium and calcium carbonates does not provide this enhancement and activity.

Statement of Invention

Thus in its broadest aspect, this invention provides a process for converting carbon monoxide and hydrogen to hydrocarbons which comprises contacting the carbon monoxide and hydrogen at a temperature ranging from about 175°C to about 400°C and a pressure ranging from about 5 bar to about 500 bar with an iron-base Fischer-Tropsch catalyst wherein said catalyst is dispersed as a slurry in an inert organic solvent and wherein additionally sodium carbonate, potassium carbonate, barium carbonate or mixtures thereof are also dispersed as a slurry in the inert organic solvent.

Description of the Preferred Embodiments

In the instant solvent phase process the catalyst, appropriately ground to the requisite particle size, is added to an inert

solvent and then syngas is bubbled therethrough, thus contacting the catalyst and maintaining the catalyst in the slurry phase. Alternatively, mechanical mixing may also be utilized to maintain the catalyst in the slurry phase and improve contact of the catalyst with the syngas.

5 The catalyst utilized in the present process comprises an iron-based Fischer-Tropsch catalyst. These catalysts are well known in the art and comprise basically a matrix of iron oxide with additional catalytically active materials from the transition metals or promoters from Group 1A (alkali metals), Group 2A (alkaline earth metals), Group
10 3A, Group 4A, the rare earth series and the actinide series. Preferably the catalyst utilized in the instant process will comprise iron and at least one other metal from the transition metal series. Most specifically, the preferred catalyst will comprise iron, manganese and zinc.

 Typically, the catalysts used herein are in unsupported form,
15 although they may be supported in a suitable inert support such as silica, alumina, silica-alumina, etc. The catalysts are prepared in typical fashion. For example, the preparation of an unsupported catalyst is typically prepared by co-precipitating the requisite metals and subsequently calcined at elevated temperatures. Typically the calcined
20 catalyst is in reduced in hydrogen prior to utilization as a catalyst. When supported catalyst materials are used, the inert support is typically impregnated with aqueous solutions of the appropriate catalytic metals, dried, calcined at an elevated temperature and then reduced in hydrogen prior to utilization. Prior to utilization, the catalyst,
25 either supported or unsupported, is crushed to a powder of sufficient fineness to allow the catalyst to be maintained as a slurry under operating conditions.

 When the preferred iron-manganese-zinc catalyst is utilized, it is preferably utilized in the unsupported form in most cases. In
30 this preferred catalyst, typically, the concentration of iron ranges from about 15 to about 50 percent by weight measured as a metal and exclusive of any support utilized, the manganese ranges from about 15 to

about 50 percent by weight measured as a metal and exclusive of any support utilized, and the zinc ranges from about 2 to about 10 percent by weight measured as a metal exclusive of any support utilized. While it is indicated that the metals herein are measured as metals, it is understood that they may be in existence in the catalyst in various oxidation states, combined with each other and with oxygen in various forms.

The additives which are supplied to the slurry phase in the instant process comprise potassium carbonate, sodium carbonate, barium carbonate or mixtures thereof. These materials are readily available in solid form from commercial sources and this solid, dried form will be ground to a suitably fine powder which can then be added to the slurry phase. Particle sizes of both catalysts and then additives which are to be added to the slurry phase are not critical, and the optimum size for maintaining a slurry under the operating conditions can be readily obtained by suitable experiments by one skilled in the art.

The slurry phase is composed of an inert organic solvent, catalyst particles, additive particles, reactants and products. The inert organic solvent is a solvent that does not react with the syngas or the products under reaction conditions. Another limitation on the inert solvent is that it must be liquid at the temperatures and pressures of operation of the syngas reaction. For example, a wax which is solid at room temperature but which melts at fairly low temperatures and is thus liquid at the operating temperature and pressure of the reaction would be a suitable inert solvent. Suitable inert solvents comprise among others, alkanes, alkenes, alkanols, phenols, benzenes and siloxanes which are liquid at the syngas reaction temperature and pressure.

The carbonate additives will typically be found present in the slurry system at a weight ratio of carbonate to catalyst ranging from about 0.005 to about 0.5, preferably from about 0.01 to about 0.2 and most preferably from about 0.015 to about 0.15.

In carrying out the instant process the inert solvent may first be added to the reactor and then the catalyst and additive added thereafter, or preferably the inert solvent and the catalyst plus additive can be slurried together and then be added to the reactor. The reactor would then be heated to the operating conditions and syngas passed through the slurry. Typical reaction temperatures range from about 175°C to about 400°C, preferably from about 200°C to about 350°C. Typical reaction pressures range from about 5 to about 500 bar, preferably from about 5 to about 200 bar, and typical feed rates include gaseous hourly space velocities ranging from about 500 to about 10,000 l/l/hr. A wide range of carbon monoxide to hydrogen can be used in the feed. For example, a carbon monoxide to hydrogen ratio ranging from about 1:2 to about 3:1 is generally suitable, although other ratios may be utilized.

The product of the instant invention will comprise primarily alkanes, alkenes and a smaller proportion of alkanols. Typically, the product carbon numbers will be in the lower range, i.e. C₁ to C₁₀. A substantial portion of the product will be alkenes, particularly lower carbon number alkenes such as C₂-C₄. The process of the instant invention, including preparation of the preferred catalyst composition, will be further described below by the following illustrative embodiment which is provided for illustration and is not to be construed as limiting the invention.

Illustrative Embodiments

The following example illustrates the typical preparation of the preferred catalyst utilized in the instant process. One hundred eighty grams of Fe(NO₃)₂·9H₂O, 160 grams of Mn(NO₃)₂ (50% solution), and 13 grams of Zn(NO₃)₂ were placed in a 2 liter beaker and distilled water was added sufficient to bring the total volume to 1 liter. A one molar solution of sodium carbonate was prepared by placing 150 grams of Na₂CO₃ and 1.5 liters of distilled water in a 2 liter beaker.

The contents of both beakers were heated to 85°C and then added to separatory funnels. The solutions were added to a 4 liter beaker containing 800 ml of distilled water at 65°C. The solutions were added at a rate such that a pH of 6.5 was maintained in the 4 liter beaker. After addition, the resultant material heated to 85°C and held for 20 minutes.

The solution was filtered, while hot, in a large Buchner funnel. The residue was reslurried with 1.5 liters of warm water and filtered again. The reslurry procedure was repeated 10 times.

The residue remaining after final filtration was dried in a vacuum oven at 125°C and 20" overnight and then calcined at 300°C for four hours.

Fifteen ml of the above catalyst, which was crushed to 20-30 mesh was placed in a glass tube and reduced under hydrogen for 20 hours at 325°C. The catalyst was then taken into a dry box and crushed to a fine powder (less than 100 mesh).

To carry out the instant slurry phase reaction, approximately 15 ml of the above described catalyst (in crushed powder form) was added to a 300 ml Hasteloy B autoclave, along with the appropriate amount of a carbonate additive. One hundred fifty ml of NEODENE® 18 (C₁₈ linear alpha olefin) was added to the autoclave. The autoclave was then sealed, flushed with syngas, then heated and pressurized to the operating conditions. The reaction was then started, and results are shown in Table 1 for various additives. Examples 1-3 illustrate additives within the scope of the instant process. Examples A and B are comparative examples utilizing other additives.

Table I. Silyry Phase Syngas Reactions
 Fe/Mn/Zn Catalysts^a + Additives (A) in NEODENE 18
 275°C, 900 psig (1H₂:2CO), 2500 GHSV

Example	Additives ^b (A) (wt%) ^b	% Syngas Conversion	Molar Selectivity (%)					
			C ₁ Methane Methanol	C ₂ Ethene/ Ethane Ethanol	C ₃ Propene/ Propane Propanol	C ₄ Butene/ Butane Butanol	C ₂ -C ₄	C ₅ ⁺
1	Na ₂ CO ₃ 5.8	38.1	6.7 0.3	10.4 3.0 0.8	2.9 3.2 0.1	18.7 8.9 0.1	50.7	42.0
2	K ₂ CO ₃ 2.4	35.0	11.4 1.1	7.9 3.5 0.2	11.8 4.3 0.0	6.3 11.4 0.1	45.5	42.0
3	BaCO ₃ 3.6	48.4	10.7 1.3	6.8 5.7 0.9	11.7 0.6 0.4	12.8 6.8 0.0	45.7	41.2
A	MgCO ₃ 12.3	9.6	9.7 1.2	10.8 1.4 1.5	7.4 2.0 0.5	14.4 12.6 0.4	51.0	38.2
B	Ca(NO ₃) ₂ 4.3	12.1	6.8 0.7	9.5 1.0 1.2	1.9 0.0 0.0	3.2 12.6 1.0	30.4	62.2
C	None	18.2	6.9 0.7	9.8 0.3 0.6	0.0 1.8 0.1	18.7 9.8 0.6	41.7	50.6

a. Catalyst composition: 25wt% Fe, 25wt% Mn, 3wt% Zn.
 b. Wt% of additive is based on amount of catalyst.

When silicon oil, mineral oil, and NEODOL® 25-3T (an ethoxy-
lated linear alcohol having a carbon number ranging from C₁₂ to about
C₁₅ and having about 3 EO groups per molecule) are utilized as the inert
solvent to provide the slurry phase, results comparable to above will be
5 obtained.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A process for converting carbon monoxide and hydrogen to hydrocarbons which comprises contacting the carbon monoxide and hydrogen at a temperature ranging from about 175°C to about 400°C and a pressure ranging from about 5 bar to about 500 bar with an iron-based Fischer-Tropsch catalyst wherein said catalyst is dispersed as a slurry in an inert organic solvent and wherein additionally sodium carbonate, potassium carbonate, barium carbonate or mixtures thereof are also dispersed as a slurry in the inert organic solvent.
2. The process of Claim 1 wherein the Fischer-Tropsch catalyst comprises iron and at least one other transition metal.
3. The process of Claim 1 wherein the catalyst comprises iron, manganese and zinc.
4. The process of Claim 3 wherein the concentration of the iron ranges from about 15 to about 50 percent by weight measured as the metal exclusive of any support, the manganese ranges from about 15 to about 50 percent by weight measured as the metal exclusive of any support and the zinc ranges from about 2 to about 10 percent by weight measured as the metal exclusive of the support.
5. The process of Claims 1, 2 or 3 wherein the temperature ranges from about 200°C to about 350°C and the pressure ranges from about 5 bar to about 200 bar.



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6. The process of Claims 1, 2 or 3 wherein the inert solvent is selected from the group consisting of alkanes, alkenes, alkanols, siloxanes, and mixtures thereof which are liquid at the contacting temperature and pressure.

7. The process of Claims 1, 2 or 3 wherein the weight ratio of carbonate to catalyst ranges from about 0.005 to about 0.5.

8. The process of Claims 1, 2 or 3 wherein the weight ratio of carbonate to catalyst ranges from about 0.01 to about 0.2.

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